15 Nov 1996

Dynamics of an Adsorbed Patch and a Model for Spreading of Films of Ultralow Thicknesses

Partho Neogi

Missouri University of Science and Technology, neogi@mst.edu

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P. Neogi
Chemical Engineering Department, University of Missouri-Rolla, Rolla, Missouri 65409-1230

(Received 8 April 1966; accepted 13 August 1996)

The dynamics of ultrathin films of liquids with vanishing 3D volatility, on solid surfaces, has been modeled by assuming that the films can be taken to be adsorbed patches spreading under surface diffusion. When the phase behavior of the adsorbed films is taken into account, it is seen that a vapor patch will spread without limits and evolve into a Gaussian profile. For a liquid film which has low 2D volatility, a patch will appear to equilibrate and the surface ahead will remain dry. This is the ''pancake,'' a case where a wetting liquid stops spreading. The spreading kinetics is generally seen to be the usual square-root-of-time type, although exceptions are also seen. A simple case of non-Fickian diffusion has been included, but fails to give anticipated results at least in a simple model. © *1996 American Institute of Physics.* [S0021-9606(96)50543-X]

INTRODUCTION

The kinetics of spreading of patches of liquids on a smooth surface have been reported[1–6] quite extensively in recent years. De Gennes and co-workers[7] have predicted that even wetting liquids will not spread on a solid surface provided that the solid surface ahead of the drop remained dry. Such drops are mesoscopic in scale, and are flat and thin. One key feature in their analysis is the importance of the length scale of $(A_H/\gamma)^{1/2}$, where A_H is Hamaker constant and γ is the surface tension of the liquid. Usual values of $A_H = 10^{-14}$ ergs and γ=25 dyn/cm lead to a value of 0.2 nm for this length scale which characterizes the thicknesses of drops and most often the stable drops that have been observed are only one or two molecules thick in the middle, although exceptions exist.

We list some results of interest here. For polydimethyl siloxane it was found that the liquid was stratified, showing one to three layers[1–5] (although larger drops have also been reported) which remain stationary over a long time. For a two-tier system both layers spread such that the extent of spreading was proportional to square root of time, with the liquid in upper tier spreading no faster than the liquid in the lower tier. For squalane no stratification was observed and the extent of spreading was clearly proportional to square root of time.[5] For some cases involving polydimethyl siloxane[6] the rate of spreading was proportional first to t^{-1} (that is the extent of spreading was proportional to ln t), then decreased faster than that for some time, and eventually became proportional to $t^{-1/2}$. The last stage is obviously the more common result. These powers were not calculated in this work, but appear to be approximately so in their Fig. 3. The very interesting results obtained for liquids which exhibit long range order, are omitted from present discussions.

Many attempts at modeling the system have been reported[8–12] and they are often based on some form of diffusion with Langevin equation as the starting point. They predict extents of spreading to be proportional to $(t \ln t)^{1/2}$, $t^{1/2}$, and to t, under various conditions, because of which there is some attempt to separate Fickian effects from the ''non-Fickian'' ones. In stratified systems, there is also an emphasis on writing separate governing equations for every layer. Some of the results are not available in closed form.

There is a different set of results that also need to be discussed in this connection. Marmur and Lelah[13] have observed experimentally water drops spreading on glass. They report that a film of ultralow thickness proceeds ahead of the bulk of the drop and interacts with the edges. This leads to differences in the rates of spreading when the shapes of a finite solid surface are changed. Teletzke *et al.*[14] have modeled the system by using disjoining pressures in the thin films in the form of $-K_n/h^n$, where they have used the index n as obtained from experimental results. Whereas $n = 3$ in usual thin films, $n = 1$ in ultrathin films, and the use of such an index does lead eventually to an explanation of the observations made by Marmur and Lelah.[13] The important feature here is that Neogi and Miller[15] have shown that the expression for viscous flow under disjoining pressure for $n = 1$, is functionally the same if this film is assumed to be a polymolecular adsorbed film moving under surface diffusion.

It is evident from the previous discussion that researchers have entered a new domain of ultralow films which are thinner and different in properties than Derjaguin–Frumkin thin films. The dynamics of such films are not fully established and are even contradictory in some of their predictions. It is also apparent that some of the features of the ultralow films can be modeled as polymolecular adsorbed films moving under surface diffusion. Analytical solutions are obtained here for the first time. Solutions to problems in cylindrical coordinates are virtually nonexistent.[16,17] That is, we know very little about dynamics of surface diffusion on a solid surface (or for that matter, diffusion in a cylinder under radial symmetry), a problem which is important in its own right. The solution sheds light on the temporal evolution of the patch, and in the present problem it is necessary to know what the classical approach actually predicts in the way of relating the extent of spreading to time. It is only then we can

separate Fickian and non-Fickian effects, and not on the basis of solutions in one dimension.

No references to stratification are made. In one case the patch is assumed to be a vapor. In the second case the patch is assumed to be a liquid with a transition to vapor at a particular liquid density (surface adsorbed concentration), which makes it a moving boundary problem. Only a case where the spreading patch reaches equilibrium (pancake) is solved. Finally a simple case on non-Fickian diffusion is analyzed. Among these we are able to predict most experimentally observed behaviors.

A VAPOR PATCH

It is a single phase problem, and the conservation equation is

$$\frac{\partial \Gamma}{\partial t} = \frac{D_s}{r}\frac{\partial}{\partial r}\left(r \frac{\partial}{\partial r}\Gamma \right), \tag{1}$$

where D_s is the surface diffusivity. The initial and boundary conditions are

(i) $\Gamma = \Gamma_0, \quad r \leqslant R,$

$= 0, \quad r > R$

at $t = 0$, and

(ii) $\Gamma \to 0 \quad$ as $\quad r \to \infty,$

(iii) $\dfrac{\partial \Gamma}{\partial r} = 0 \qquad$ at $r = 0.$

The problem is solved through Hankel transform,[18] defined as

$$\overline{\Gamma} = \int_0^\infty \Gamma r J_0(rp)\, dr, \tag{2}$$

where J_0 is the Bessel function of zero order. Equation (1) becomes

$$\frac{\partial}{\partial t}\overline{\Gamma} = -p^2 D_s \overline{\Gamma},$$

with the solution

$$\overline{\Gamma} = A \exp(-p^2 D_s t). \tag{3}$$

The initial condition is transformed to yield the expression for the constant A. The inverse from Tranter[18] is

$$\Gamma = \Gamma_0 R \int_0^\infty J_1(Rp) e^{-p^2 D_s t} J_0(rp)\, dp, \tag{4}$$

where J_1 is Bessel function of order one. If we know the total moles, then $M = \pi R^2 \Gamma_0$. Using this to eliminate Γ_0 and taking the limit that R tends to zero, we get

$$\Gamma = \frac{M}{\pi}\int_0^\infty p e^{-p^2 D_s t} J_0(rp)\, dp \tag{5a}$$

and

$$\Gamma = \frac{M}{8\pi D_s t}\exp\left(-\frac{r^2}{4 D_s t} \right) \tag{5b}$$

after evaluating the integral.[19] If we assume now in the experiments the contact line is measured at $r = r^*$, where the surface concentration is the lowest measurable concentration Γ^*, then by substituting in to Eq. (5b) we get

$$r^* = \sqrt{(C_1 t + C_2 t \ln t)}, \tag{6}$$

where $C_1 = 4D_s \ln(M/\Gamma^* 8\pi D_s)$ and $C_2 = -4D_s$. Up to moderate times one has a square root of time type of dependence (it is important to keep in mind that Γ^* is very small making C_1 very large). Although a $(t \ln t)^{1/2}$ term like in Eq. (6), is also seen in molecular simulations,[12] its role here is quite different and unimportant.

A LIQUID PATCH

It is now assumed that the patch is a liquid. When its density drops to Γ_∞, the saturated liquid value, the film density profile suffers a discontinuity as the next available density is that of the saturated vapor. In here it is assumed that the densities of the vapor are low such that the total mass in form of vapor can be ignored, at least over the time scales of interest. The governing equation is Eq. (1) and of the boundary conditions that follow also apply here with the exception of the boundary condition (ii), which becomes

(ii) $\Gamma = \Gamma_\infty \qquad$ at $r = r_0$.

One more condition is still needed to evaluate r_0, the position of the edge of the patch, which is also the contact line. This will be provided later. Changing variables to $\xi = r/r_0, \theta = (\Gamma/\Gamma_\infty - 1)$, and

$$\tau = \int_0^t \frac{D_s\, dt'}{r_0^2}, \tag{7}$$

where $\tau = 0$ at $t = 0$. One has

$$\frac{\partial \theta}{\partial \tau} = \frac{1}{\xi}\frac{\partial}{\partial \xi}\left(\xi \frac{\partial \theta}{\partial \xi} \right), \tag{8}$$

(i) $\theta = \Gamma_0/\Gamma_\infty - 1 \qquad$ at $\tau = 0,$

(ii) $\theta = 0 \qquad$ at $\xi = 1,$

(iii) $\partial\theta/\partial\xi = 0 \qquad$ at $\xi = 0.$

Using Laplace transform (for τ) on Eq. (8) and the boundary conditions, we get

$$\overline{\theta} = (\Gamma_0/\Gamma_\infty - 1)\left[\frac{1}{s} - \frac{I_0(\xi\sqrt{s})}{s I_0(\sqrt{s})} \right], \tag{9}$$

where I_0 is the modified Bessel function of the first kind and zero order and s is the variable of the transform. Inversion through Heaviside formula leads to

$$\frac{\Gamma}{\Gamma_\infty} = 1 + \sum_{n=1}^{\infty} \frac{2}{x_n}\left(\frac{\Gamma_0}{\Gamma_\infty} - 1 \right)\frac{J_0(\xi x_n)}{J_1(x_n)} e^{-x_n^2 \tau}, \tag{10}$$

where x_n are the zeros of J_0.

The remaining boundary condition is that the mass transferred across the contact line is

$$\dot{m}=\Gamma(-\dot{r}_0)-D_s\frac{\partial\Gamma}{\partial r}\qquad \text{at } r=r_0, \tag{11}$$

in the absence of the source/sink term at the contact line.[20] In the present model $\dot{m}\simeq 0$, and the above equation becomes on rearrangement

$$\left.\frac{\partial\Gamma/\Gamma_\infty}{\partial\xi}\right|_{\xi=1}\sim-\frac{r_0\dot{r}_0}{D_s}. \tag{12}$$

Substituting from Eq. (10), one has

$$2\left(\frac{\Gamma_0}{\Gamma_\infty}-1\right)\sum_{n=1}^{\infty}e^{-x_n^2\tau}=-\frac{r_0\dot{r}_0}{D_s}. \tag{13}$$

From Eq. (7) $d\tau = d\overline{t}/Y$, where $\overline{t} = D_s t/R^2$ and $Y = (r_0/R)^2$. Using these, Eq. (13) becomes

$$2\left(\frac{\Gamma_0}{\Gamma_\infty}-1\right)\sum_{n=1}^{\infty}e^{-x_n^2\tau}=-\frac{1}{Y}\frac{dY}{d\tau}. \tag{14}$$

Integrating once from the limit of $Y = 1$ at $\tau=0$, one has an integral equation

$$4\left(\frac{\Gamma_0}{\Gamma_\infty}-1\right)\sum_{n=1}^{\infty}\frac{1}{x_n^2}(1-e^{-x_n^2\tau})=-\ln Y. \tag{15}$$

This integral equation can be solved numerically. Equation (15) can be use to obtain τ vs Y. The slopes $d\tau/dY = Y^{-1}\, d\overline{t}/dY$ can be calculated numerically as a function of Y, and a numerical integration would lead to Y as a function of $\overline{t}$.

Now, the relation between τ and Y in Eq. (7) makes it clear that if Y tends to a finite limit at infinite times, then in the same limit τ will go to infinity. Substituting these limits into Eq. (15), one has the equilibrium extent of spreading

$$Y_\infty=\exp\left[4\left(\frac{\Gamma_0}{\Gamma_\infty}-1\right)\sum_{n=1}^{\infty}x_n^{-2}\right]=\exp\left[-0.9353\left(\frac{\Gamma_0}{\Gamma_\infty}-1\right)\right]. \tag{16}$$

One can also make a material balance that $\pi R^2\Gamma_0 = \pi[r_0(\infty)]^2\Gamma_\infty$, which together with Eq. (16) predicts that the initial concentration Γ_0 is unique, which appears to be absurd. Actually, the system of equations provide no real solution for Γ_0, and this exercise underlines the fact that the present assumption that there is no significant 2D evaporation ($\dot{m}\approx 0$) at large times is not valid. The solution itself has an error of ord($\dot{m}$), and the error in $\pi R^2\Gamma_0 - 2\pi\int_0^{r_0} r\Gamma\, dr$ is of the order of the integral of $\dot{m}$ over time. Now even though $\dot{m}$ is small, the integral will not be small at large times (say times of the order of $\dot{m}^{-1}$) and the predicted equilibrium will never occur as the solution will fail. What would happen is that the radius will increase from R to values close to $r_0(\infty)$ [the value of which is predicted in Eq. (16)] relatively quickly, and then slowly dissipate mass by the 2D vaporization. No equilibrium will actually be reached.

An approximate expression for Y as a function of $\overline{t}$, can be obtained from Eq. (15) by considering only the first zero. Other zeros are much larger and do not contribute significantly to the summation. This leads to

$$\tau=-\frac{1}{x_1^2}\ln\left\{1-\frac{\ln Y}{(4/x_1^2)[(\Gamma_0/\Gamma_\infty)-1]}\right\}, \tag{17}$$

where $x_1 = 2.405$, the smallest zero. Differentiating both sides leads to

$$d\overline{t}=\frac{1}{4\left(\frac{\Gamma_0}{\Gamma_\infty}-1\right)}\frac{dY}{1-\frac{x_1^2}{4[(\Gamma_0/\Gamma_\infty)-1]}\ln Y}. \tag{18}$$

At short times $Y\sim 1$. Substituting into Eq. (18) and integrating, one has

$$\overline{t}=\frac{1}{4[(\Gamma_0/\Gamma_\infty)-1]}(Y-1). \tag{19}$$

It can be rewritten as

$$r_0^2=R^2+\left(\frac{\Gamma_0}{\Gamma_\infty}-1\right)\frac{4D_s t}{R^2}, \tag{20}$$

which shows the classical square-root-of-time type of behavior. At large times $Y\sim Y_\infty$. Expanding ln Y in Taylor's series about Y_∞, retaining the first two terms, using the form for Y_∞ from Eq. (16) where only the first zero is used, and integrating, one has

$$\overline{t}=-\frac{Y_\infty}{x_1^2}\ln(Y-Y_\infty)+\text{const}, \tag{21}$$

which can be rewritten as

$$r_0^2=r_0(\infty)^2-[r_0(\infty)^2-R^2]e^{-x_1^2D_s t/r_0(\infty)^2}. \tag{22}$$

The important feature in Eq. (22) is that it is neither square-root-of-time type nor a simple exponential decay.

NON-FICKIAN DIFFUSION

The diffusivity in three dimensions is defined as the integral of the velocity autocorrelation function from time $t = 0$ to $t = \infty$. However, the autocorrelation function decreases very fast with time to zero, and the integral at even short times is very close to the value at infinite times. If the times are even shorter, then a memory-dependent diffusion and non-Fickian effects result.[21] The governing equations are

$$\frac{\partial c}{\partial t}=\frac{1}{r}\frac{\partial}{\partial r}\left[\int_0^t\mu(t-t')r\frac{\partial c}{\partial r}(r,t')dt'\right], \tag{23}$$

where c is the three-dimensional concentration and the memory is defined through the relaxation function μ, which is also the velocity autocorrelation function. At large times, Fickian diffusion results with the diffusivity given by

$D=\int_0^\infty \mu(t)dt$. Thus the non-Fickian effect is the generalization of Fickian which includes behaviors at short times. At short times Eq. (23) yields[22]

$$\frac{\partial^2 c}{\partial t^2} \simeq \frac{\mu_0}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right), \tag{24}$$

where $\mu_0 = \mu(0)$.

If it is assumed that the same structure of equations hold in surface diffusion, then one can replace Eq. (1) with Eq. (24) with Γ replacing c, to study non-Fickian diffusion of this kind which is expected to arise at short times. The boundary conditions and the method of solution follow Eq. (1) as before. The solution is

$$\Gamma = \frac{M}{\pi R}\int_0^\infty J_1(Rp)\cos(p\sqrt{\mu_0}t)J_0(rp)dp. \tag{25}$$

However, unlike the previous example, no solution is obtained in the limit of R tending to zero. This happens because the governing equation, Eq. (24), is a wave equation. If initially a mass is deposited at a point, then it denotes a wave of a very high crest. The immediate response is for it to fall into a trough, which translates into negative concentrations, which are inadmissible here.

At large values of R, one could get an asymptotic expansion by first expanding[19] $J_1(Rp)$ for large R and then carrying out the integrations. These integrations are not simple to organize,[23] and show that the solution is $r^{-1/2}F$, where the function F is complicated, and represents waves traveling with a constant speed of $\sqrt{\mu_0}$. The location of the contact line is surmised to be at $r_0 = R + t\sqrt{\mu_0}$. Thus the square-root-of-time-dependence is broken, but the $(\ln t)$ ''non-Fickian'' dependence[6] seen in the experiments at short times, is not recovered.

The non-Fickian model presented here is a very simple one, where the continuity amongst different ideas presented here have been emphasized. Among many complications that can arise, is the fact that $\mu(0)$ may neither be finite nor nonzero, etc.

DISCUSSION

The effort to model ultrathin films by treating them as adsorbed layers, is not new but appear not to have been studied systematically. However, there are many works reported on equilibrium aspects, of which only the review-cum-research paper of Hirasaki[24] is cited.

It has been shown here that ultrathin films can be treated quite successfully as polymolecular adsorbed films spreading under surface diffusion. In particular it is possible to show that if the film is liquidlike and does not easily form adsorbed vapor phase ahead of it, then a pancake shaped equilibrium patch will evolve. It is being assumed here that the liquids under consideration are nonvolatile in 3D sense. When the adsorbed liquid film does not easily give rise to an adsorbed vapor film ahead of it, then it is not volatile in two dimensions, abbreviated as 2D nonvolatile. Thus, an equilibrium patch is formed only if the liquid is 2D nonvolatile, in which case the solid surface ahead of the drop remains dry. This stipulation is the same as that made by de Gennes and co-workers,[7] that equilibrium pancakes of thin films form if the solid surface ahead remains dry.

It is also seen that if the adsorbed liquid easily gives rise to an adsorbed vapor, or that the film is in vapor phase to begin with, then no equilibrium will result. Of course such adsorbed films are 2D volatile. Cazabat and co-workers used this phrase to explain why squalane did not form a pancake,[5] but their explanation that squalane was more vaporlike does not help to distinguish such behavior from 3D volatility.

Finally, it is seen that the present formalism is also able to quantify the dynamics quite well. Together with the expected square-root-of-time behavior, other dependencies are also observed. The main feature of course, is that we present the dynamics of surface diffusion of patches for the first time, including the one where equilibrium is attained. An attempt is made to analyze non-Fickian diffusion along the lines available in three-dimensional systems, and the result falls short of expectations at least using the simples model for relaxation.

It is interesting to note that the present model predicts that the patch has to be a liquid to give rise to a pancake, and the liquids (includes polydimethyl siloxane) which give rise to pancakes are seen to be stratified in the experiments where the pancake formation was investigated. One expects stratification at high densities (''liquid state'') from the nature of oscillatory solvation forces. However, the experiments at equilibrium show that these oscillatory forces do not exist in thin films of polymer melts.[25] Consequently, the stratification seen is probably a nonequilibrium effect, brought about by some existing forces that favor stratification. However, as the experiments of Cazabat and co-workers show, stratification at times, is caused by very specific chemistry of the system and this feature is not discussed any further.

It is important to show how stratified systems can be handled in the present model. First, one postulates the existence of several liquid states as Γ falls, connected with first order phase transitions until eventually the vapor phase is realized. At these transitions the surface concentrations fall discontinuously. Second, every phase has its own diffusivity, and jump material balances[20] have to be applied at the junctions. This multiple moving boundary problem is difficult to solve even numerically and the approximate solutions given by de Gennes and Cazabat[8] are implicit, but simple and has been shown to be quite good[1] and there does not seem to be much point in solving the more complicated system. It is useful to note that their model, for the case when there are only two strata ($R_3 = 0$) shows that the sum of the areas covered by the two strata is a constant, as appropriate in a model that assumes incompressibility. However, at short times the equations become very similar to Eq. (18) (with respect to the term in logarithm), which is a diffusion equation.

The key feature in the present work has been to show that a simple model of an adsorbed patch moving under a constant diffusivity goes a long way in quantifying many of the phenomena observed in ultrathin films.

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